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(54) Title: CATALYST FOR REMOVING CARBON MONOXIDE IN HYDROGEN RICH GAS ACCORDING TO WATER GAS SHIFT REACTION

(57) Abstract: A catalyst for removing carbon monoxide (CO) in a hydrogen rich gas according to a water gas shift reaction is provided. This catalyst includes platinum and rhenium supported as catalyst metals on a rutile titania support. This catalyst provides a high CO conversion at a relatively low reaction temperature between 200 °C and 300 °C and is excellent in cost/performance due to a reduction in amount of supported platinum. It is preferred that a weight ratio of an amount of supported platinum to an amount of supported rhenium is in a range of 3:1 to 1:1, and particularly 3:2. For example, an apparatus using this catalyst is expected as a hydrogen source for a fuel cell of generating electricity from a reaction between hydrogen and oxygen.

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## DESCRIPTION

CATALYST FOR REMOVING CARBON MONOXIDE IN  
HYDROGEN RICH GAS ACCORDING TO WATER GAS SHIFT  
REACTION

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## TECHNICAL FIELD

The present invention relates to a catalyst for selectively removing carbon monoxide (CO) in a hydrogen rich gas according to water gas shift reaction, apparatus for treating the hydrogen rich gas with the catalyst to provide a gas having a higher hydrogen concentration than the hydrogen rich gas, and a method of removing CO from the hydrogen rich gas with the use of the catalyst.

## 15 BACKGROUND ART

In recent years, proton-exchange membrane fuel cells having advantages of a low operation temperature, high power density, reductions in size and weight and an accelerated start-up time receive widespread attention as a fuel cell power generation system of the next generation, and are expected in applications to cars, compact electric generators, home cogeneration devices and so on. In the proton-exchange membrane fuel cells, a perfluorosulfonic acid based polymer film is used as a proton-conductive solid electrolyte, and can be operated at a temperature between 50 °C to 100 °C.

25 However, since a hydrogen rich gas generated by a reaction between steam and a hydrocarbon fuel or an alcohol fuel such as methanol is used as a hydrogen source for the fuel-cell power generation system, there is a problem that the proton-exchange membrane fuel cells easily receive damages by the presence of impurities in the hydrogen rich

gas. In particular, carbon monoxide (CO) in the hydrogen rich gas gives considerable damages to platinum used as electrode materials. When the CO concentration in the hydrogen rich gas exceeds a threshold value, the power generation capacity lowers.

5 To avoid the damages of platinum caused by carbon monoxide, it is proposed to set up a CO removing device for removing carbon monoxide in the hydrogen rich gas such that the CO concentration becomes about 1 % or less, and a device for selective oxidation reaction of further reducing the CO concentration to 50 PPM or less.

10 By the way, the CO removing device uses a catalyst for selectively removing carbon monoxide in the hydrogen rich gas according to a water gas shift reaction. As this kind of catalyst, for example, Japanese Patent Gazette No. 3215680 discloses a catalyst for a water gas shift reaction, which is characterized in that platinum and rhenium are supported on a  
15 support of zirconia. There are advantages this catalyst shows a higher catalyst activity than a conventional copper-zinc catalyst, and a deterioration with time of the catalyst performance is relatively small.

However, there is a problem that the CO conversion of the catalyst according to the water gas shift reaction rapidly decreases under  
20 conditions of a reaction temperature of 250°C or less and a high space velocity, i.e., a large supply amount of the hydrogen rich gas. This means that a higher reaction temperature is needed to efficiently remove carbon monoxide in the hydrogen rich gas. In addition, since a relatively large amount of platinum must be supported on zirconia to obtain a desired  
25 catalyst performance, there is still plenty of room for improvement in cost / performance of the catalyst.

## SUMMARY OF THE INVENTION

Therefore, a primary concern of the present invention is to provide

a catalyst for removing carbon monoxide in a hydrogen rich gas according to water gas shift reaction, which has the capability of providing an improved CO conversion at a relatively low reaction temperature between 200°C and 300°C and excellent cost/performance due to a reduction in amount of platinum used in the catalyst, while maintaining the advantages of a conventional catalyst characterized in that rhenium and platinum are supported on zirconia. That is, the catalyst of the present invention includes platinum and rhenium supported as catalyst metals on a rutile titania support.

It is preferred that an amount of supported platinum is in a range of 0.05 to 3 % with respect to catalyst weight. In addition, it is preferred that an amount of supported rhenium is in a range of 0.01 to 10 % with respect to catalyst weight.

It is also preferred that a weight ratio of an amount of supported platinum to an amount of supported rhenium is in a range of 3:1 to 1:1.

A further concern of the present invention is to provide a method of removing carbon monoxide in a hydrogen rich gas according to the water gas shift reaction with use of the catalyst described above. In this method, it is preferred that carbon monoxide is removed from the hydrogen rich gas at a temperature between 250 °C and 300 °C. In this case, it is possible to achieve a remarkably high CO conversion, as compared with the conventional catalysts. In addition, it is preferred that a CO conversion of the catalyst according to the water gas shift reaction is 60 % or more when it is measured at a reaction temperature of 250 °C, with respect to a mixture gas obtained by mixing a hydrogen rich gas containing about 12% of carbon monoxide with water such that a mole ratio of  $H_2O/CO$  is substantially equal to 4.3, in the case that an amount of the hydrogen rich gas treated per unit weight of supported platinum is in a range of 5000 to 5500 [cc/(min · g(Pt))].

Another concern of the present invention is to provide an apparatus for treating a hydrogen rich gas containing carbon monoxide according to the water gas shift reaction with use of the catalyst described above. That is, this apparatus comprises the catalyst including platinum and rhenium supported as catalyst metals on a rutile titania support; a  
5 reaction vessel having a catalyst room, in which the catalyst is housed; a gas flow channel for supplying the hydrogen rich gas into the catalyst room; a heater for heating the catalyst at a temperature suitable for the water gas shift reaction; a gas outlet for providing a gas having a higher  
10 hydrogen concentration than the hydrogen rich gas, which is obtained by the water gas shift reaction between the catalyst and the hydrogen rich gas in the catalyst room.

These and still other objects and advantages of the present invention will become more apparent from the following detail description and preferred examples of the present invention, referring to the attached  
15 drawings.

The present disclosure relates to subject matters contained in Japanese Patent Application No. 2002-111232, which was filed on April 12, 2002, the disclosure of which is expressly incorporated herein by  
20 reference in its entirety.

#### BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a graph showing relationships between a reaction temperature and a CO conversion with respect to catalysts of Examples 1 to 4 of the  
25 present invention;

FIG. 2 is a graph showing relationships between a reaction temperature and a CO conversion under another condition with respect to the catalysts of Examples 1 to 4 of the present invention;

FIG. 3 is a graph showing relationships between a reaction temperature

and a CO conversion with respect to catalysts of Examples 2, 5 and 6 of the present invention and Comparative Example 1;

FIG. 4 is a graph showing relationships between a reaction temperature and a CO conversion under another condition with respect to the catalysts of Examples 2, 5 and 6 of the present invention and Comparative Example 1;

FIG. 5 is a graph showing relationships between a reaction temperature and a CO conversion with respect to catalysts of Examples 2, 7 and 8 of the present invention;

FIG. 6 is a graph showing relationships between a reaction temperature and a CO conversion under another condition with respect to the catalysts of Examples 2, 7 and 8 of the present invention; and

FIG. 7 is a schematic diagram of an apparatus for treating a hydrogen rich gas with a catalyst for water gas shift reaction according to a preferred embodiment of the present invention.

### BEST MODE FOR CARRYING OUT THE INVENTION

A catalyst for removing carbon monoxide in a hydrogen rich gas of the present invention is explained in detail below.

The catalyst of the present invention is characterized in that platinum and rhenium are supported on a rutile titania support. Rutile titania as the support can be prepared by, for example, dissolving titanium ores as a starting material in sulfuric acid, heating and calcining a resultant solution. In addition, titania-coated particles obtained by coating rutile titania on particles of a metal oxide such as alumina, zirconia, silica-alumina, zeolite, magnesia, niobium oxide, zinc oxide, chromium oxide or the like may be used as the support.

It is preferred that an amount of supported platinum is in a range of 0.05 % to 3 % with respect to catalyst weight. When the amount of

supported platinum is less than 0.05 %, there is a fear that the catalyst does not show a sufficient catalyst activity in the water shift gas reaction for converting carbon monoxide (CO) in the hydrogen rich gas into carbon dioxide (CO<sub>2</sub>). On the other hand, when the amount of supported platinum is more than 3 %, it is not expected to further increase the catalyst activity. Therefore, in such a case, a deterioration in cost/performance of the catalyst cost comes into a problem. In addition, since a methanation reaction that is a hydrogen consumption reaction caused at a high reaction temperature region is enhanced, there is a tendency of lowering the hydrogen concentration obtained.

By the way, a support containing rutile titania as the main component may be used as the rutile titania support. In this case, it is preferred that a content of rutile titania in the support of the catalyst is 80 % or more. In addition, it is preferred that a specific surface area of the rutile titania support is 10 [m<sup>2</sup>/g] or more. When the rutile titania content and/or the specific surface area is within the above range(s), it is possible to achieve a remarkably high CO conversion by the water gas shift reaction at the temperature of 250 °C or 300 °C, as compared with the case of using a support containing anatase titania as the main component.

In the present invention, it has been found that the catalyst activity can be remarkably improved at a relatively low temperature between 200 °C and 300 °C by supporting both of rhenium and platinum on the support. It is preferred that an amount of supported rhenium is in a range of 0.01 % to 10 % with respect to catalyst weight. When the amount of supported rhenium is less than 0.01 %, it becomes difficult to sufficiently obtain an additive effect of rhenium to the water gas shift reaction. On the other hand, when the amount of supported rhenium is more than 10 %, the additive effect of rhenium to the catalyst activity is saturated, so that the

cost/performance of the catalyst may deteriorate.

In addition, it is preferred that a weight ratio of an amount of supported platinum to an amount of supported rhenium is in a range of 3:1 to 1:1, and particularly 3:2.

5       Next, a method of producing the above-described catalyst of the present invention is explained. This method comprises a first step of supporting rhenium on the rutile titania support, and a second step of supporting platinum on the rutile titania support after the first step. For example, an aqueous solution of a rhenium salt is added to rutile titania, and then water in a resultant mixture is evaporated with agitation to obtain  
10       a first intermediate product. The first intermediate product is dried by heating, so that rhenium is supported on the support. Subsequently, an aqueous solution of a platinum salt is added to the support on which rhenium is already supported. Water in a resultant mixture is evaporated  
15       with agitation to obtain a second intermediate product. The second intermediate product is dried by heating, so that platinum is supported on the support with the already supported rhenium.

After the rutile titania supporting platinum and rhenium thereon is pulverized and calcined, an obtained calcining body is press-molded to  
20       obtain a pellet. By pulverizing the pellet to a particle size of 0.5 mm to 1 mm, the catalyst of the present invention is obtained, which is characterized in that rhenium and platinum are supported on rutile titania.

The catalyst of the present invention can be produced by methods other than the above-described method. For example, the catalyst may  
25       be produced by supporting platinum first on rutile titania and then supporting rhenium on the support. Alternatively, the catalyst of the present invention may be produced by adding aqueous solutions of platinum and rhenium salts to rutile titania at a time. Therefore, in this case, platinum and rhenium can be simultaneously supported on the



support.

However, it is particularly preferred to supporting rhenium first on rutile titania and then support platinum on the support. According to this method, it is possible to stably obtain a great advantage that a CO  
5 conversion of the catalyst according to the water gas shift reaction is 60 % or more when it is measured at a reaction temperature of 250 °C, with respect to a mixture gas obtained by mixing a hydrogen rich gas containing about 12% of carbon monoxide with water such that a mole ratio of  $H_2O/CO (=S/C)$  is substantially equal to 4.3, in the case that an  
10 amount of the hydrogen rich gas treated per unit weight of supported platinum is in a range of 5000 to 5500 [cc/(min · g(Pt))], and specifically about 5300 [cc/(min · g(Pt))]. The effectiveness of this particularly preferred production method of the present invention will be further clearly understood by Examples shown below.

15 By the way, in this technical field, a "space velocity" (SV, [1/h]) that is "an amount of the hydrogen rich gas treated per unit volume of the catalyst" is usually used to discuss the catalyst performance. However, when catalysts with different amounts of supported platinum are used, it is difficult to accurately evaluate a difference in CO conversion between  
20 those catalysts under a constant "SV" condition. In other words, even when the SV condition is constant, a higher CO conversion can be achieved by simply increasing the amount of supported platinum. Therefore, in the present invention, as a precondition for discussing the CO conversion of the catalyst, a definition of "an amount ( $SV_{(Pt)}$ , [cc/(min ·  
25 g(Pt))]) of the hydrogen rich gas treated per unit weight of platinum supported on the support" is used. Thereby, it is possible to accurately perform a reasonable comparison in CO conversion between the catalysts with different amounts of supported platinum. Of course, when the amount of supported platinum is constant, it is possible to accurately

evaluate the CO conversion under the constant SV condition.

For example, the amount of the hydrogen rich gas treated per unit weight of supported platinum can be determined by the following procedure. When an amount of supported platinum is 3 % by weight, and a weight of the catalyst used for evaluation is 6.4 g, a weight of platinum in the catalyst is 0.19 g ( $=6.4 \text{ g} \times 3.0/100$ ). When an amount of a hydrogen rich gas supplied to evaluate the catalyst performance is 1000 [cc/min], "the amount of the hydrogen rich gas treated per unit weight of supported platinum" is approximately 5300 [cc/(min · g(Pt))] ( $=1000 \text{ [cc/min]} \div 0.19$  [g]).

Next, a preferred embodiment of an apparatus of treating a hydrogen rich gas containing carbon monoxide according to the water gas shift reaction with use of the above-described catalyst of the present invention is explained below. As shown in FIG. 7, this apparatus 1 has a reaction vessel 2, which is provided with a gas inlet 3, a first catalyst room 10 for a reforming catalyst 11, a second catalyst room 20 for the catalyst 21 of the present invention, a third catalyst room 30 for a CO selective oxidation catalyst 31, and a gas outlet 6. For example, steam and methane gas or propane gas are supplied into the reaction vessel 2 through the gas inlet 3. The methane gas or propane gas is reacted with steam by the help of the reforming catalyst 11 in the first catalyst room 10, while the reforming catalyst is being heated by a burner, to generate a hydrogen rich gas containing hydrogen (approx. 72%), carbon monoxide (approx. 10%), carbon dioxide (approx. 15%) and methane (approx. 2%).

The hydrogen rich gas generated in the first catalyst room 10 is then sent to the second catalyst room 20 through a first gas flow channel 4. In the second catalyst room 20, the water gas shift reaction between carbon monoxide in the hydrogen rich gas and steam is performed in the presence of the catalyst of the present invention to obtain a resultant gas

containing 1% or less of carbon monoxide. The catalyst 21 housed in the second catalyst room 20 can be heated at a temperature suitable for the water gas shift reaction, preferably 250 to 300 °C by the burner heating. In this embodiment, the catalysts (21, 31) housed in the second and third catalyst rooms (20, 30) can be heated by the burner heating, as in the case of the reforming catalyst 11 of the first catalyst room 10. Alternatively, additional heaters may be formed to separately heat these catalysts. In addition, it is preferred that an average particle size of the catalyst 21 housed in the second catalyst room 20 is within a range of 0.1 to 3.0 mm.

The gas provided from the second catalyst room 20, which has a higher hydrogen concentration and a lower CO concentration than the hydrogen rich gas provided from the first catalyst room 10, can be used as a fuel gas. However, in the present apparatus, the gas is further sent to the third catalyst room 30 through a second gas flow channel 5. The concentration of carbon monoxide in the gas is further reduced to 50 ppm or less by the CO selective oxidation catalyst 31 in the third catalyst room 30. The air required for the selective oxidation reaction is mixed to the gas supplied from the second catalyst room 20 at the second gas flow channel 5. As a result, the gas provided from the gas outlet 6 has a lower carbon-monoxide concentration than the gas provided from the second catalyst room 20. The treatment apparatus of this embodiment can be used as a hydrogen source for a fuel cell of generating electricity from a reaction between hydrogen and oxygen.

By the way, in the above explanation, the hydrogen rich gas was generated from the methane gas or propane gas with use of the reforming catalyst 11 in the first catalyst room 10 according to the steam reforming process. Alternatively, as the method of generating the hydrogen rich gas from a hydrocarbon fuel such as town gas, propane, butane, methanol

or the like, the autothermal reforming process or the partial reforming process may be used. When using the steam reforming process, the hydrogen rich gas contains hydrogen as the main constituent, carbon monoxide, carbon dioxide and methane, and the hydrogen concentration is within a range of 65% to 80%. When using the autothermal reforming process, the hydrogen rich gas contains hydrogen as the main constituent, carbon monoxide, carbon dioxide, methane and nitrogen, and the hydrogen concentration is within a range of 50% to 55%. In addition, when using the partial reforming process, the hydrogen rich gas contains hydrogen as the main constituent, carbon monoxide, carbon dioxide, methane and nitrogen, and the hydrogen concentration is within a range of 35% to 45%. In the present specification, the hydrogen rich gas is not limited to a gas containing 50% or more of hydrogen, and may contain hydrogen as the main constituent.

15

## EXAMPLES

(Examples 1 to 6 and Comparative Example 1)

Using a calcining furnace, a reagent of rutile titania (a reference catalyst supplied by the Catalysis Society of Japan) was subjected to a calcining treatment wherein it was heated to a temperature of 500 °C in one hour in an air flow of 60 ml/min, and kept at the temperature for one hour, and thereby a rutile titania support of Example 1 was prepared.

A required amount of the obtained rutile-titania support was put on an evaporation pan located in a hot water bath. Then pure water was added to the support and they were mixed intimately. Next, an aqueous solution of ammonium perrhenate ( $\text{NH}_4\text{ReO}_4$ ) (manufactured by NACAL TESQUE INC.) was added to the evaporation pan. Pure water was further added to reach a predetermined concentration. By agitating a resultant mixture on the evaporation pan located in the hot water bath, water

included in the resultant mixture was evaporated, while a metal salt depositing on a wall of the evaporation pan was being washed away with pure water into the bottom of the evaporation pan. After the evaporation, the mixture was further dried at about 100 °C for at least 12 hours, so that  
5 rhenium was supported on rutile titania.

Next, a required amount of the support with rhenium thereon was put on an evaporation pan located in a hot water bath. Then pure water was added to the support and they were mixed intimately. Next, a dinitrodiamine-platinum(II) nitric acid solution (manufactured by TANAKA  
10 KIKINZOKU KOGYO K.K.) was added to the evaporation pan. Pure water was further added to reach a predetermined concentration. By agitating a resultant mixture on the evaporation pan located in the hot water bath, water included in the resultant mixture was evaporated in two hours, while a metal salt depositing on a wall of the evaporation pan was  
15 being washed away with pure water into the bottom of the evaporation pan. After the evaporation, the mixture was further dried at about 100 °C for at least 15 hours, so that platinum was supported on the support with the already supported rhenium.

After the dried mixture was pulverized into powder in a mortar, the  
20 powder was heated to a temperature of 500 °C in one hour in an air flow of 60 ml/min, and calcined at the temperature for one hour. In addition, the calcined powder was pressed at a pressure of 3600 kg/cm<sup>2</sup> for 10 seconds by use of a manual hydraulic compressing machine to obtain pellets having a required shape. Those pellets were pulverized into particles of  
25 which diameter is in the range between 1.4 mm and 2.0 mm. Thus, the catalyst for removing carbon monoxide of Example 1 was obtained, which is characterized in that platinum and rhenium are supported on rutile titania.

To obtain the catalysts of Examples 1 to 6, the additive amounts of

dinitrodiamine platinum and ammonium perrhenate were controlled such that the amounts of platinum and rhenium listed in Table 1 are supported on the support. That is, in Examples 1 to 4, under a condition that the amount of supported platinum is 1% with respect to catalyst weight, the amount of supported rhenium was changed in a range of 3:1 to 1:3 of a weight ratio of the amount of supported platinum to the amount of supported rhenium. In Examples 5 and 6, under a condition that the weight ratio of the amount of supported platinum to the amount of supported rhenium is 3:2, the amount of supported platinum was changed, as listed in Table 1.

A catalyst of Comparative Example 1 was prepared by the following method. That is, using the calcining furnace, a reagent of zirconia (a reference catalyst supplied by the Catalysis Society of Japan) was subjected to a calcining treatment wherein it was heated to a temperature of 500 °C in one hour in an air flow of 60 ml/min, and kept at the temperature for one hour, and thereby the zirconia of Comparative Example 1 was prepared. Then, according to a substantially same method as Example 1, the catalyst of Comparative Example 1 was obtained by supporting platinum and rhenium on the zirconia support such that the amount of supported platinum is 3 % and the amount of supported rhenium is 2 % with respect to catalyst weight.

Table 1

wt%	Support	Supported amounts		Pt : Re
		Pt	Re	
Example 1	rutile titania	1	0.33	3:1
Example 2	rutile titania	1	0.67	3:2
Example 3	rutile titania	1	1	1:1
Example 4	rutile titania	1	3	1:3
Example 5	rutile titania	3	2	3:2
Example 6	rutile titania	0.5	0.33	3:2
Comparative Example 1	zirconia	3	2	3:2

With respect to the catalysts of Examples 1 to 6 and Comparative Example 1, catalyst performance was evaluated under conditions shown below.

- 5 (1) Influence of a ratio of platinum to rhenium (under a condition that an amount of supported platinum is constant)

With respect to each of the catalysts of Examples 1 to 4, 6 cc of the catalyst was filled in a reaction tube. The catalyst was heated to a temperature of 500 °C in one hour in a flow of a hydrogen rich gas having  
10 a composition of H<sub>2</sub>(74.3%), CO(11.7%), CO<sub>2</sub>(13.6%) and CH<sub>4</sub>(0.4%), and kept at the temperature for one hour to carry out a reduction treatment. Subsequently, the hydrogen rich gas was mixed with water such that a mole ratio of H<sub>2</sub>O/CO(=S/C) is substantially equal to 4. 3. A resultant mixture of the hydrogen rich gas and water was supplied to the reaction  
15 tube at a space velocity (SV) of 5000 [1/h] or 10000 [1/h]. Under these conditions, carbon monoxide in the hydrogen rich gas was removed according to a water gas shift reaction at a reaction temperature of 200°C. After the reaction was stabilized, a treated gas was collected at an outlet of the reaction tube and analyzed by means of gas chromatography with a  
20 thermal conductivity detector and a flame ionization detector to determine a conversion of CO into CO<sub>2</sub>. Similarly, the CO conversion was determined at different reaction temperatures of 250°C, 300°C, 350°C and 400°C. Results are shown in FIGS. 1 and 2.

FIG. 1 shows a reaction temperature dependency of the CO  
25 conversion measured at the space velocity of 5000 [1/h] with respect to each of the catalysts of Examples 1 to 4. This graph shows that the highest catalyst performance (CO conversion) at the reaction temperatures of 200 °C and 250 °C that are in a low temperature region in the present experiment conditions is achieved at a ratio of platinum to  
30 rhenium between 3:1 and 1:1. That is, when the ratio of platinum to

rhenum is 3:2, about 75 % of the CO conversion was achieved at the reaction temperature of 200 °C, and a high CO conversion of more than 90% was achieved at the reaction temperature of 250 °C. When the reaction temperature exceeds 350 °C, a deviation from the equilibrium curve (without consideration of the methanation reaction) increased due to the methanation reaction.

FIG. 2 shows a reaction temperature dependency of the CO conversion measured at a higher space velocity of 10000 [1/h] with respect to each of the catalysts of Examples 1 to 4. The reaction temperature dependency shown in this graph has similarity with FIG. 1. However, in the reaction temperature range between 200 °C and 300 °C, the catalyst performance obtained at the ratio of platinum to rhenum of 3:1 is substantially equal to the catalyst performance obtained at the ratio of platinum to rhenum of 3:2. That is, when the ratio of platinum to rhenum is 3:2 (or 3:1), about 37% of the CO conversion was achieved at the reaction temperature of 200°C, and about 70% of the CO conversion was achieved at the reaction temperature of 250°C. In addition, at the reaction temperature of 300°C, a high CO conversion of more than 80% was achieved.

(2) Influence of an amount of supported platinum (under a condition that a ratio of platinum to rhenum is constant)

With respect to each of Examples 2, 5, 6 and Comparative Example 1, 6.4 g of the catalyst were filled in a reaction tube. The catalyst was heated to a temperature of 500 °C in one hour in a flow of a hydrogen rich gas having a composition of H<sub>2</sub>(74.4%), CO(11.7%), CO<sub>2</sub>(13.5%) and CH<sub>4</sub>(0.4%), and kept at the temperature for one hour to carry out a reduction treatment. Subsequently, the hydrogen rich gas was mixed with water such that a mole ratio of H<sub>2</sub>O/CO (=S/C) is substantially equal to 4. 3. A resultant mixture of the hydrogen rich gas



and water was supplied to the reaction tube such that an amount ( $SV_{(Pt)}$ ) of the hydrogen rich gas treated per unit weight of supported platinum is 2587 [cc/(min · g(Pt))] or 5173 [cc/(min · g(Pt))]. Under these conditions, carbon monoxide in the hydrogen rich gas was removed according to the water gas shift reaction at a reaction temperature of 200°C. After the reaction was stabilized, a treated gas was collected at an outlet of the reaction tube and analyzed by means of gas chromatography with a thermal conductivity detector and a flame ionization detector to determine a conversion of CO into CO<sub>2</sub>. Similarly, the CO conversion was determined at different reaction temperatures of 250°C, 300°C, 350°C and 400°C. Results are shown in FIGS. 3 and 4.

FIG. 3 shows a reaction temperature dependency of the CO conversion measured with respect to each of the catalysts of Examples 2, 5 and 6 having different amounts of supported platinum within a range of 0.5 % to 3 %, under conditions that the ratio of platinum to rhenium is 3:2 (constant) and the amount ( $SV_{(Pt)}$ ) of the hydrogen rich gas treated per unit weight of supported platinum is 2587 [cc/(min · g(Pt))]. For example, in Example 2, since the amount of supported platinum is 1 % with respect to catalyst weight, the catalyst performance was evaluated at 1667 [1/h] of the space velocity to satisfy the condition that the amount ( $SV_{(Pt)}$ ) of the hydrogen rich gas treated per unit weight of supported platinum is 2587 [cc/(min · g(Pt))]. Similarly, in Example 5, since the amount of supported platinum is 3 % with respect to catalyst weight, the catalyst performance was evaluated at 5000 [1/h] of the space velocity to satisfy the condition that the amount ( $SV_{(Pt)}$ ) of the hydrogen rich gas treated per unit weight of supported platinum is 2587 [cc/(min · g(Pt))].

This graph shows that the highest catalyst performance (CO conversion) at the reaction temperature of 200 °C that is the lowest temperature in the present experiment conditions is obtained at 1% of the

amount of supported platinum, and particularly the CO conversion approximately reaches the equilibrium curve (shown by dotted line in FIG. 3) at the reaction temperature of 250 °C. In addition, when the catalyst of Comparative Example 1 (zirconia support) is compared with the catalyst of Example 5 having the same amounts of supported platinum and rhenium as Comparative Example 1, a difference in CO conversion therebetween is small at the reaction temperature of 250 °C. However, the difference therebetween considerably increases at the reaction temperature of 200 °C. As described below, the difference in catalyst performance between the catalysts of Example 5 and Comparative Example 1 will be more clearly understood from results of the experiment performed under a more severe test condition.

FIG. 4 shows a reaction temperature dependency of the CO conversion measured with respect to each of the catalysts of Examples 2, 5 and 6 having different amounts of supported platinum within a range of 0.5 % to 3 %, under conditions that the ratio of platinum to rhenium is 3:2 (constant) and the amount ( $SV_{(Pt)}$ ) of the hydrogen rich gas treated per unit weight of supported platinum is 5173 [ $cc/(min \cdot g(Pt))$ ] (without consideration of significant figures). When the significant figures are considered, the amount ( $SV_{(Pt)}$ ) is approximately 5300 [ $cc/(min \cdot g(Pt))$ ].

This graph shows that the highest catalyst performance (CO conversion) at the reaction temperatures of 200 °C and 250 °C that are in a low temperature region in the present experiment conditions is obtained at 1 % of the amount of supported platinum, and particularly the CO conversion exceeds 85 % at the reaction temperatures of 250 °C. In addition, when the catalyst of Comparative Example 1 (zirconia support) is compared with the catalyst of Example 5 having the same amounts of supported platinum and rhenium as Comparative Example 1, there is a considerable difference in CO conversion at the low reaction temperature

region (200°C, 250°C).

(Example 7)

A required amount of a rutile-titania support prepared by the same method as Example 1 was put on an evaporation pan located in a hot water bath. Then pure water was added to the support and they were mixed intimately. Next, a dinitrodiamine-platinum(II) nitric acid solution (manufactured by TANAKA KIKINZOKU KOGYO K.K.) was added to the evaporation pan. Pure water was further added to reach a predetermined concentration. By agitating a resultant mixture on the evaporation pan located in the hot water bath, water included in the resultant mixture was evaporated for two hours, while a metal salt depositing on a wall of the evaporation pan was being washed away with pure water into the bottom of the evaporation pan. After the evaporation, the mixture was further dried at about 100 °C for at least 15 hours, so that platinum was supported on rutile titania.

Next, a required amount of the support with platinum thereon was put on an evaporation pan located in a hot water bath. Then pure water was added to the support and they were mixed intimately. Next, an aqueous solution of ammonium perrhenate ( $\text{NH}_4\text{ReO}_4$ ) (manufactured by NACALAI TESQUE INC.) was added to the evaporation pan. Pure water was further added to reach a predetermined concentration. By agitating a resultant mixture on the evaporation pan located in the hot water bath, water included in the resultant mixture was evaporated for two hours, while a metal salt depositing on a wall of the evaporation pan was being washed away with pure water into the bottom of the evaporation pan. After the evaporation, the mixture was dried, calcined, pressed and pulverized, as in the case of Example 1, so that the catalyst of Example 7 was obtained, which is characterized in that platinum and rhenium are supported on rutile titania. In Example 7, an amount of supported

platinum is 1 % with respect to catalyst weight, and an amount of supported rhenium is 0.67 % with respect to catalyst weight. Therefore, a weight ratio of the amount of supported platinum to the amount of supported rhenium is 3:2.

5 (Example 8)

A required amount of a rutile-titania support prepared by the same method as Example 1 was put on an evaporation pan located in a hot water bath. Then pure water was added to the support and they were mixed intimately. Next, a dinitrodiamine-platinum(II) nitric acid solution  
10 (manufactured by TANAKA KIKINZOKU KOGYO K.K.) and an aqueous solution of ammonium perrhenate ( $\text{NH}_4\text{ReO}_4$ ) (manufactured by NACAL TESQUE INC.) were added to the evaporation pan. Pure water was further added to reach a predetermined concentration. By agitating a resultant mixture on the evaporation pan located in the hot water bath,  
15 water included in the resultant mixture was evaporated, while a metal salt depositing on a wall of the evaporation pan was being washed away with pure water into the bottom of the evaporation pan. After the evaporation, the mixture was further dried at about 100 °C for at least 12 hours, so that platinum and rhenium were supported on rutile titania at the same time.  
20 After the evaporation, the mixture was dried, calcined, pressed and pulverized, as in the case of Example 1, so that the catalyst of Example 8 was obtained, which is characterized in that platinum and rhenium are supported on rutile titania. In Example 8, an amount of supported platinum is 1 % with respect to catalyst weight, and an amount of  
25 supported rhenium is 0.67 % with respect to catalyst weight. Therefore, a weight ratio of the amount of supported platinum to the amount of supported rhenium is 3:2.

(3) Influence of a method of producing the catalyst

With respect to each of the catalysts of Examples 2 to 7 and 8, 6 cc

of the catalyst was filled in a reaction tube. The catalyst was heated to a temperature of 500 °C in one hour in a flow of a hydrogen rich gas having a composition of H<sub>2</sub> (72.9%), CO (12.1%), CO<sub>2</sub> (14.1%) and CH<sub>4</sub> (0.9%), and kept at the temperature for one hour to carry out a reduction treatment.

5 Subsequently, the hydrogen rich gas was mixed with water such that a mole ratio of H<sub>2</sub>O/CO (=S/C) is substantially equal to 4. 3. The resultant mixture of the hydrogen rich gas and water was supplied to the reaction tube at a space velocity (SV) of 5000 [1/h] or 10000 [1/h]. Under these conditions, carbon monoxide in the hydrogen rich gas was removed  
10 according to the water gas shift reaction at a reaction temperature of 200°C. After the reaction was stabilized, a treated gas was collected at an outlet of the reaction tube and analyzed by means of gas chromatography with a thermal conductivity detector and a flame ionization detector to determine a conversion of CO into CO<sub>2</sub>. Similarly,  
15 the CO conversion was determined at different reaction temperatures of 250°C, 300°C, 350°C and 400°C. Results are shown in FIGS. 5 and 6.

FIG. 5 shows a reaction temperature dependency of the CO conversion measured at the space velocity of 5000 [1/h] with respect to each of the catalysts of Examples 2, 7 and 8. That is, this graph shows a  
20 difference in CO conversion among the catalysts produced by the method (Example 2) of supporting rhenium first and then platinum on the support, the method (Example 7) of supporting platinum first and then rhenium on the support, and the method (Example 8) of supporting rhenium and platinum on the support at the same time, under a condition that the ratio  
25 of platinum to rhenium is 3:2. From this result, it is concluded that the catalyst produced by the method of Example 2 demonstrates the highest catalyst performance (CO conversion) at the reaction temperatures of 200 °C and 250 °C that are in a low temperature region in the present experiment conditions.

FIG. 6 shows a reaction temperature dependency of the CO conversion measured at a higher space velocity of 10000 [1/h] with respect to each of the catalysts of Examples 2, 7 and 8. This graph shows that the catalyst produced by the method of Example 2 demonstrates excellent catalyst performance at all of the reaction temperatures of the present experiment in despite of such a severe space velocity condition. Therefore, these results indicate that the catalyst having particularly excellent catalyst performance of the present invention can be obtained by selecting the method (Example 2) of supporting rhenium first and then platinum on rutile titania. In FIGS. 5 and 6, since a methanation reaction occurred at a high reaction temperature region of more than 350 °C, a deviation from the equilibrium curve (without consideration of the methanation reaction) increased.  
(Examples 9~12 and Comparative Example 2)

Experiments for investigating relationships between specific surface area, crystal structure of the titania support and CO conversion of the catalyst were performed. A hydrogen rich gas used in the experiments has a composition of H<sub>2</sub> (72.9%), CO (12.1%), CO<sub>2</sub> (14.1%) and CH<sub>4</sub> (0.9%). This hydrogen rich gas was mixed with water such that a mole ratio of H<sub>2</sub>O/CO (=S/C) is substantially equal to 4. 3. The resultant mixture of the hydrogen rich gas and water was supplied at a space velocity (SV) of 10000 [1/h] into a reaction vessel, in which each of catalysts of Examples 9 to 12 and Comparative Example 2 was housed. A titania content in the support, the crystal structure and the specific surface area of the titania support are shown in Table 2. The water gas shift reaction was performed at the respective temperatures of 250 °C and 300 °C in the reaction vessel to remove the carbon monoxide from the hydrogen rich gas. Results are shown in Table 2. The support used in Example 11 contains 11% of silica other than rutile titania.

The TiO<sub>2</sub> supports used in Examples 9, 10 and Comparative Example 2 are respectively JRC-TIO-3, JRC-TIO-5 and JRC-TIO-1, each of which was supplied by the Catalysis Society of Japan. In addition, the TiO<sub>2</sub> supports used in Examples 11 and 12 were manufactured by SAKAI  
 5 CHEMICAL INDUSTRY CO. LTD. and ISHIHARA SANGYO KAISHA, LTD., respectively. Amounts of supported rhenium and platinum are 2.8 wt% and 3.0 wt%, respectively.

Table 2

	CO conversion [%]		BET surface area [m <sup>2</sup> /g]	TiO <sub>2</sub> content [%]	TiO <sub>2</sub> crystal structure
	250°C	300°C			
Example 9	70.4	81.0	40	99.7	rutile
Example 10	25.8	44.5	2.6-2.7	99.9	rutile>90%
Example 11	57.9	75.7	80	89	rutile
Example 12	70.3	84.7	39	98.6	rutile
Comparative Example 2	6.9	12.3	72.6	95	anatase

10

As understood from the results of Table 2, the catalyst of each of Examples 9 to 12 exhibits a remarkably high CO conversion at the temperatures of 250 °C and 300 °C as compared with Comparative Example 2 using the anatase titania support. In addition, it is noted that  
 15 although the specific surface area of the rutile titania support of Example 10 is much smaller than that of the anatase titania support of Comparative Example 2, the catalyst performance of Example 10 is higher than that of Comparative Example 2.

## 20 Industrial Applicability

According to the present invention, by supporting platinum and rhenium on rutile titania, it is possible to provide an improved catalyst for removing carbon monoxide in a hydrogen rich gas, which has the capability of providing a high CO conversion at a relatively low reaction  
 25 temperature between 200 °C and 300 °C and excellent cost/performance

due to a reduction in amount of platinum used in the catalyst, while maintaining advantages of a conventional catalyst characterized in that rhenium and platinum are supported on zirconia. That is, the catalyst of the present invention is characterized in that platinum and rhenium are supported on rutile titania. This catalyst is particularly preferable to use for a compact fuel cell power generation system of the next generation, in which start-up and start-down operations are performed over and over again.

In addition, the treatment apparatus using the catalyst of the present invention, which has the capability of providing a remarkably high CO conversion at the relatively low temperature region, is expected as, for example, a hydrogen source for a fuel cell of generating electricity from a reaction between hydrogen and oxygen.



**CLAIMS:**

1. A catalyst for removing carbon monoxide (CO) in a hydrogen rich gas according to water gas shift reaction, said catalyst comprising platinum and rhenium supported as catalyst metals on a rutile titania support.  
5
2. The catalyst as set forth in claim 1, wherein the amount of supported platinum is in a range of 0.05 to 3 % with respect to catalyst weight.  
10
3. The catalyst as set forth in claim 1, wherein the amount of supported rhenium is in a range of 0.01 to 10 % with respect to catalyst weight.  
15
4. The catalyst as set forth in claim 1, wherein a weight ratio of supported platinum to supported rhenium is in a range of 3:1 to 1:1.
- 20 5. A method of removing carbon monoxide (CO) in a hydrogen rich gas according to water gas shift reaction with use of a catalyst comprising platinum and rhenium supported as catalyst metals on a rutile titania support.
- 25 6. The method as set forth in claim 5, wherein carbon monoxide is removed from the hydrogen rich gas at a temperature between 250 °C and 300 °C.

7. The method as set forth in claim 5, wherein a CO conversion of the catalyst according to the water gas shift reaction is 60 % or more when it is measured at a reaction temperature of 250 °C, with respect to a mixture  
5 gas obtained by mixing a hydrogen rich gas containing about 12% of carbon monoxide with water such that a mole ratio of  $H_2O/CO$  is substantially equal to 4.3, in the case that an amount of the hydrogen rich gas treated per unit weight of supported platinum is in a range of 5000 to 5500 [cc/(min · g(Pt))].

10

8. An apparatus for treating a hydrogen rich gas containing carbon monoxide with use of a catalyst for water gas shift reaction, said apparatus comprising:  
15 said catalyst including platinum and rhenium supported as catalyst metals on a rutile titania support;  
a reaction vessel having a catalyst room, in which the catalyst is housed;  
a gas flow channel for supplying the hydrogen rich gas into said catalyst room;  
20 a heater for heating said catalyst at a temperature suitable for the water gas shift reaction; and  
a gas outlet for providing a gas having a higher hydrogen concentration than the hydrogen rich gas, which obtained by the water gas shift reaction between the catalyst and the hydrogen rich gas in said catalyst room.

25

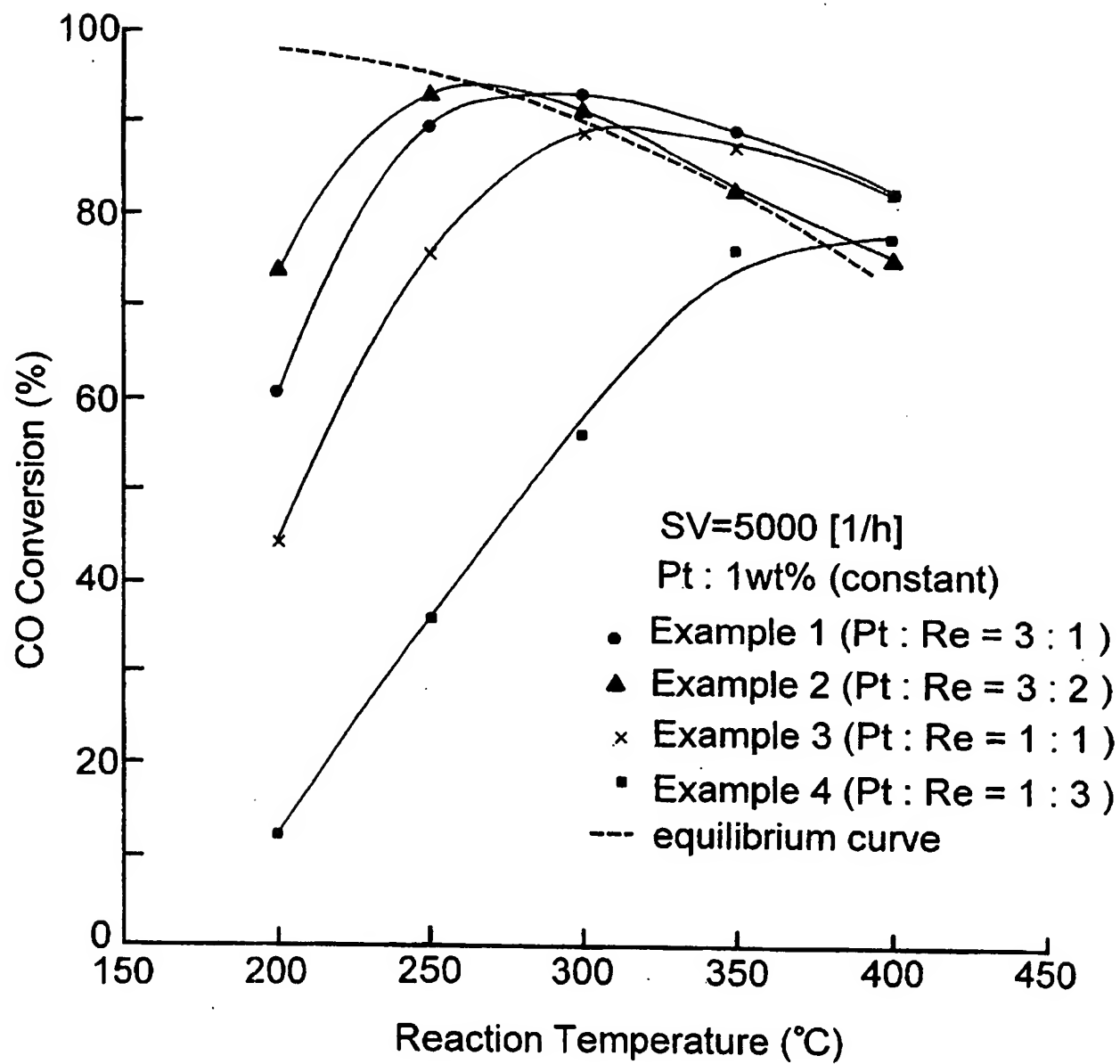
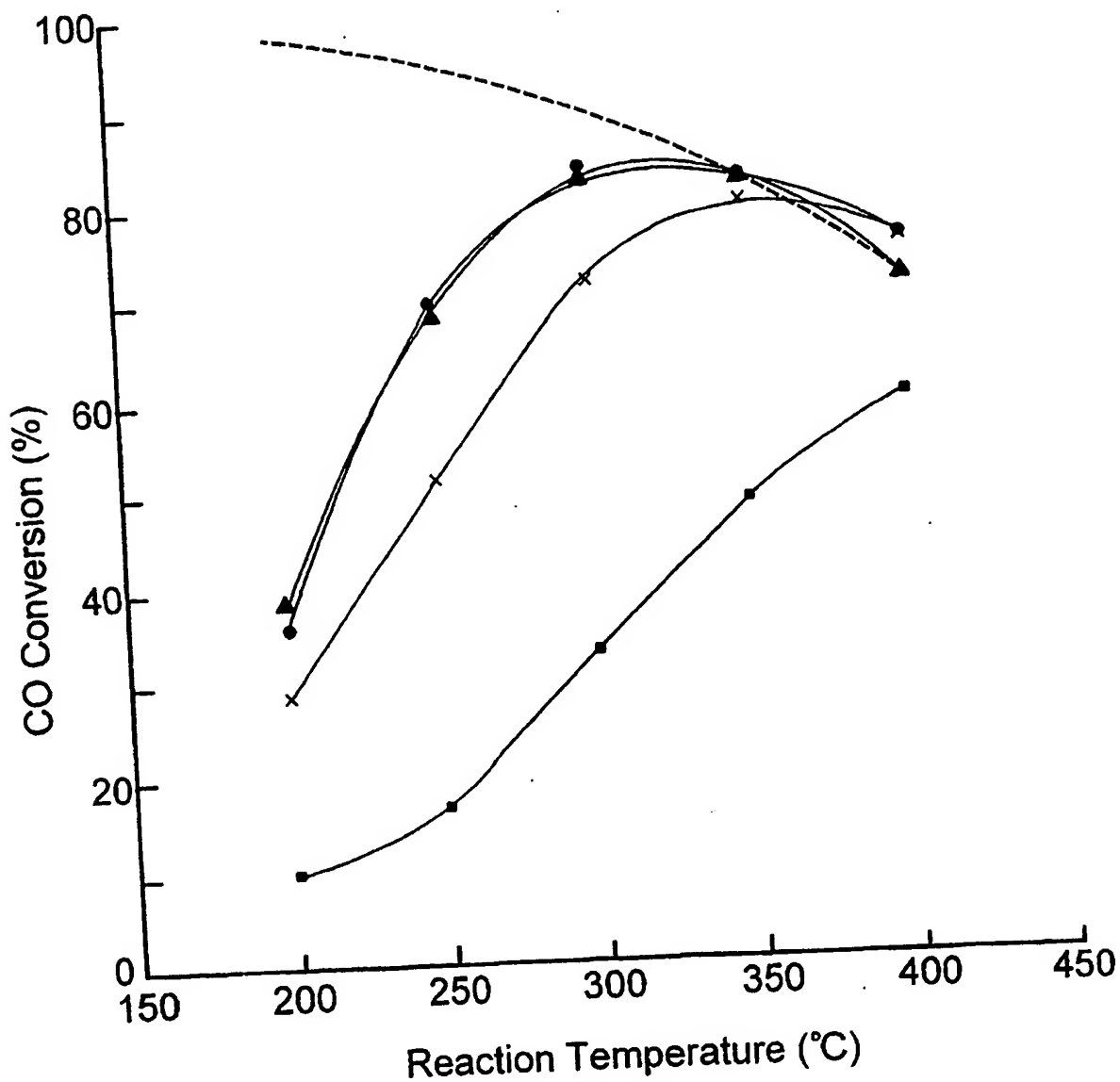


FIG. 1



SV=10000 [1/h]

Pt : 1wt% (constant)

• Example 1 (Pt : Re = 3 : 1 )

▲ Example 2 (Pt : Re = 3 : 2 )

× Example 3 (Pt : Re = 1 : 1 )

▪ Example 4 (Pt : Re = 1 : 3 )

--- equilibrium curve

**FIG. 2**

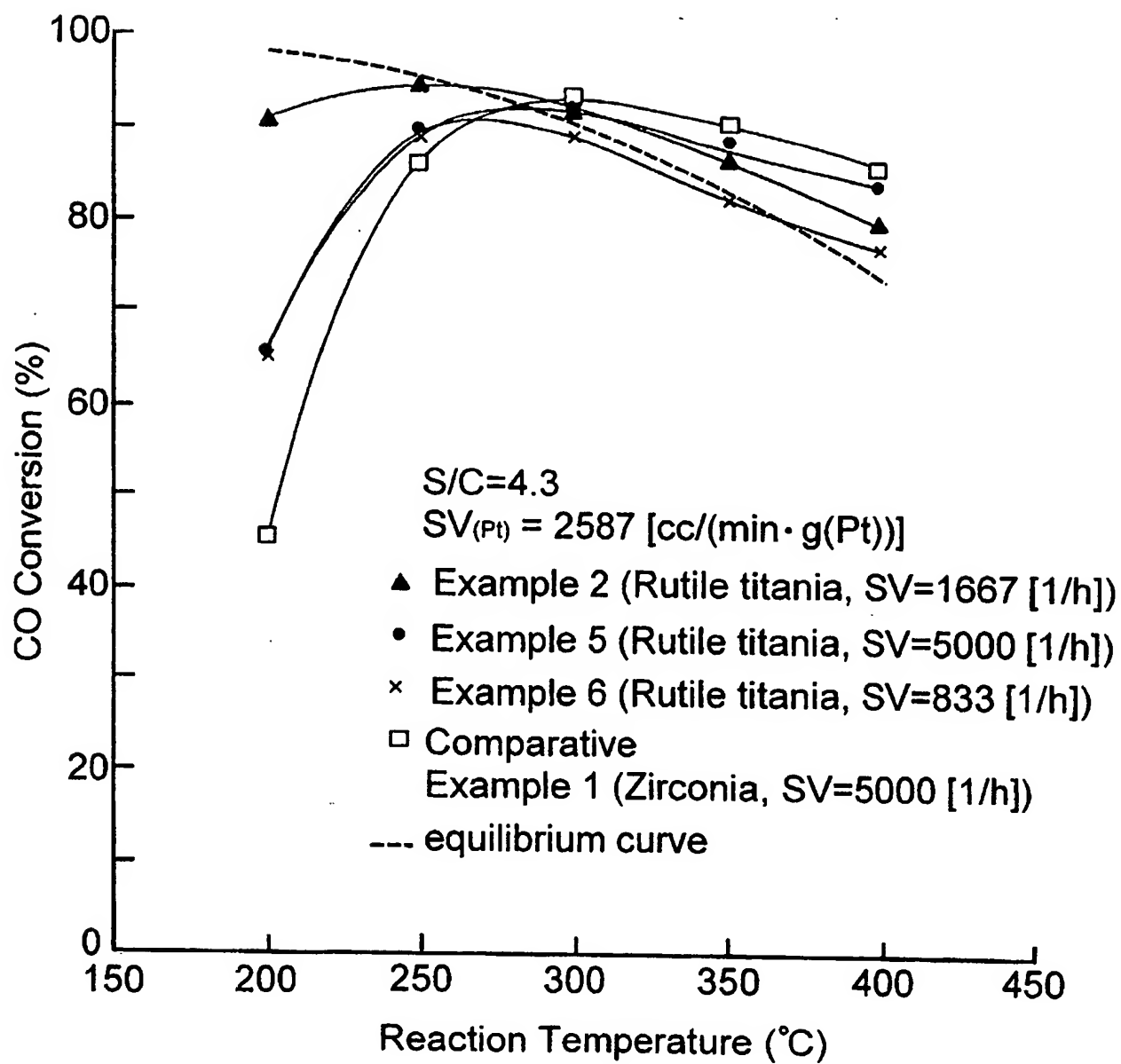


FIG. 3

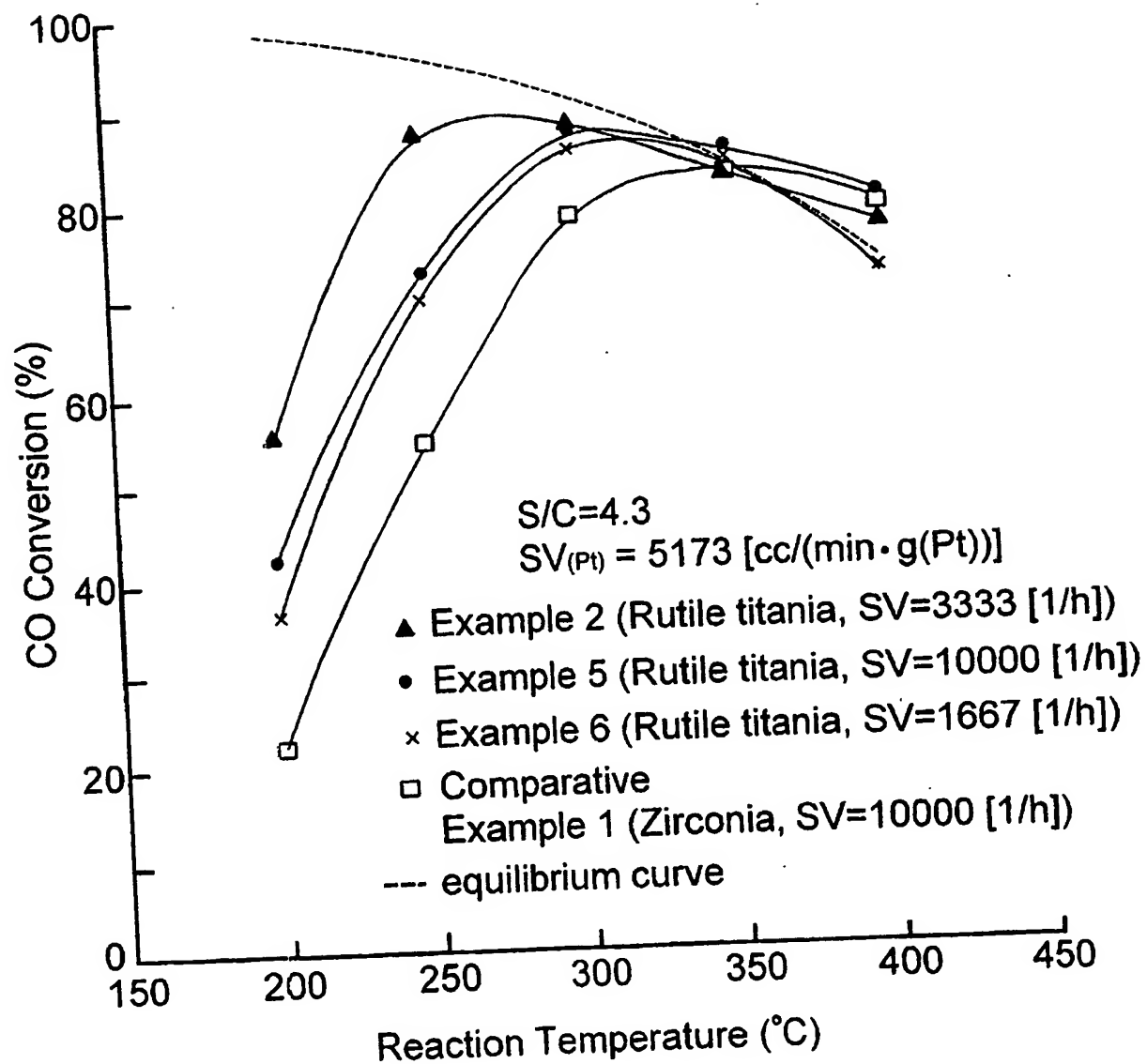
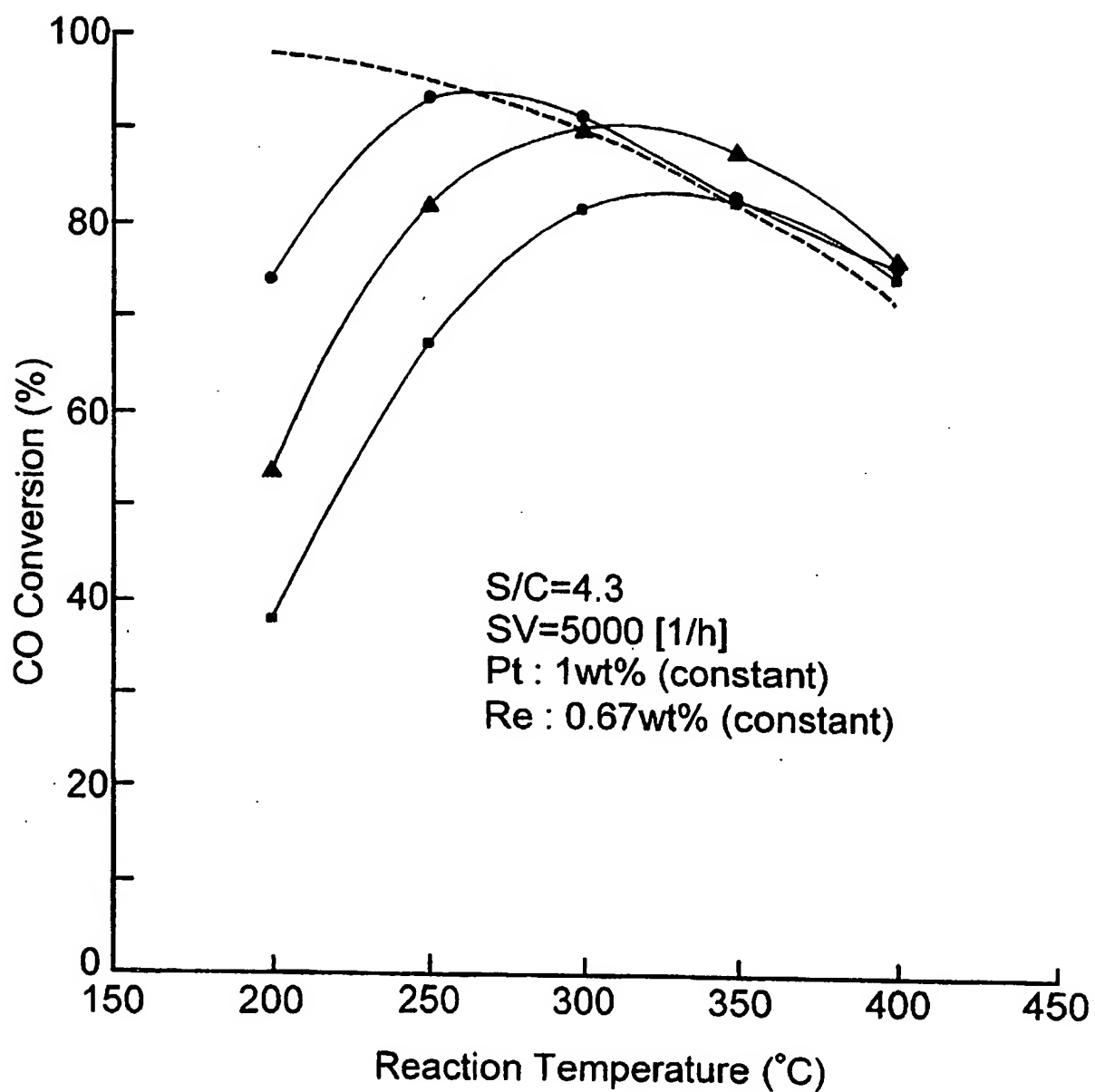


FIG. 4



- Example 2 (supporting Re first and then Pt)
- ▲ Example 7 (supporting Pt first and then Re)
- Example 8 (supporting Re and Pt at the same time)
- equilibrium curve

**FIG. 5**

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/JP 03/04645

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 B01J23/656 C01B3/40 C01B3/48 C01B3/58

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C01B H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 15, 6 April 2001 (2001-04-06) & JP 2000 342968 A (TOYOTA MOTOR CORP), 12 December 2000 (2000-12-12) abstract	1-8
A	US 5 904 913 A (STEINWANDEL JUERGEN ET AL) 18 May 1999 (1999-05-18) abstract; claim 1 --- -/--	1-8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### ° Special categories of cited documents :

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Date of the actual completion of the international search

8 July 2003

Date of mailing of the international search report

20.08.2003

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# INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>HAJIME IIDA ET AL: "LOW-TEMPERATURE WATER GAS SHIFT REACTION OVER Pt-Re CATALYSTS SUPPORTED ON ZrO<sub>2</sub> AND TiO<sub>2</sub>" ADV. IN TECH. OF MAT. PROC. J (ATM), vol. 4, no. 2, 2002, pages 62-65, XP002246871 "Presented at the 8th JAPAN/KOREA SYMPOSIUM on CATALYSIS, Osaka Prefecture University, Japan May 29, 30, 2001. Accepted: 30 November 2001". -----</p>	1-8

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 03/04645

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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			EP	0787679 A1	06-08-1997